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ON THE COMBUSTION OF CONDENSED SYSTEMS

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ON THE MECHANISM OF CATALYST ACTION
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A significant number of works [1-6] are devoted to the investigation of the mechanism of catalysis during the combustion of condensed mixtures with an ammonium perchlorate (APC) base. There is no single point of view on this question. Data by the authors of [2-4, 6] confirm a gas phase mechanism of catalyst action, while experiments [1] indicate that the place of catalyst action is the condensed phase. The theory of extremely strong catalysis in the gas phase [2] predicts a strong dependence of the effectiveness of a catalyst on its degree of dispersion. However, in the literature, there are no data on the dependence of the effectiveness of catalyst action on its dispersion.

The present work is devoted to the experimental investigation of the mechanism of catalyst action on the combustion of condensed systems using APC as a base. In the work we give the results of the investigations of catalysis of the combustion of APC and of mixtures having it as a base by using an optical microscope and an electron scanning microscope, and we also give the results of

investigations of the effect of dispersion of a catalyst on the APC combustion rate and of a model APC and polymethyl-methacrylate (PMMA) system.

The investigation of combustion surfaces of extinguished specimens with the help of a scanning electron microscope (SEM) and an optical microscope. Specimens burned at 1 atm were extinguished by a sudden drop in pressure with a break in the diaphragm dividing the large-volume evacuated container from the container in which the specimen was burned at 1 atm.

The surfaces of the extinguished fuel specimens were studied using an optical microscope and an electron scanning microscope (Cambridge Instrument Company Stereoscan) with a high magnification and a large depth of focus. These traits, distinguishing the SEM from the optical microscope, made it a powerful instrument for the study of a combustion mechanism of APC and APC-based fuels. In the American literature a whole series of works has been published on the use of an SEM for studying the structure of extinguished surfaces of specimens of APC and APC-based fuels [7-9], which explained a number of facts important for understanding the combustion mechanism of these fuels. However, the mechansim of catalyst action was not studied with the help of an SEM in these works.

The following was established as a result of the investigations conducted.

The surface of extinguished specimens composed of a stoichiometric mixture of APC (2 μm)+PMMA (3 μm)+2.0% Fe_2O_3 (4 μm) an accumulation of catalyst particles occurs. As is seen in figures 1a, b the portion of the surface which is occupied by catalyst particles (in photographs a, b it is a black color) is, in the case of specimens extinguished at 1 atm, one order greater than for the reference specimens. Catalyst particles (average measurement 10-20 μm) are connected by their bases to the surface and protrude over it. In Figure 1c the fused upper parts of the catalyst granules

Figure 1. Surface extinguished at 1 atm (a, c, d, e)
and shear surface (b) of specimens of a mixed
composition. a, c) APC (2 μm)+PMMA (3 μm)+2%
Fe_2O_3 (4 μm); d, e) without a catalyst; a, b)
obtained with the help of an optical microscope;
c, d, e) obtained with the help of an SEM.

(the white color) are visible. Their connection with the surface occurs because of their connection at the base with other catalyst particles which are in the k-phase. Catalyst particles in a fuel form a framework inside which the APC particles are located. If a tablet of APC (250-400 μm)+2.5% Fe_2O_3 is 100% decomposed, this catalyst frame is sufficiently stable and preserves its tablet form. During combustion (as opposed to decomposition) the portion of the frame which is over the combustion surface in the flame zone burns and collapses (by sampling and analyzing combustion products of the composition APC+PMMA+1% Fe_2O_3 at 1 atm, it was shown that ferric oxide burns and changes into ferric chloride). Luminous cells, which were also discovered in [6], are formed and move along the surface of the burning fuel APC+PMMA+1% Fe_2O_3. The observations described above make it possible to explain the formation of these cells.

To all appearances, catalyst particles protruding 10-20 μm over the combustion surface are the source of the luminescence. An unusually distinct catalyst frame (or casing) is visible on the extinguished surfaces of specimens of fuel with coarsely dispersed APC (250-400 μm). In this case, the catalyst particle frame with fused edges protrudes several hundred microns over the surface of APC particles, forming honeycombs inside which the APC particles are located. Apparently, the ignition and combustion of these honeycombs, beginning at a distance of several dozen microns over the k-phase surface, are the cause of the formation of luminous cells. The formation of a catalyst particle frame over the k-phase surface increases the effectiveness of its action since, as a result of such an effect, the concentration of catalyst particles in the gas phase over the combustion surface is raised substantially (by two or three orders).

With the help of an electron scanning microscope, we succeeded in explaining a number of the traits of catalysis in the k-phase which occur during the combustion, at p=1 atm, of APC (2 μm)+2% CuO mixture (the diameter of the catalyst particles was less than

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40 μm and the specific catalyst surface was ~1 m^2/g). In figures 2a, b, c a portion of the surface of the combustion of specimen APC (2 μm)+2% CuO extinguished at 1 atm is shown at different magnifications.

Figure 2. Electron-microscope photographs, obtained at different magnifications with the help of an SEM, of a portion of the surface, extinguished at 1 atm, of specimen APC (2 μm)+2% CuO.

From figure 2 it follows that: 1) catalyst particles measuring 10-20 μm accumulate on the combustion surface; 2) around catalyst particles in APC grooves are formed so that the catalyst particles are located in funnels whose diameters on the combustion surface are approximately twice as large as the diameter of the catalyst particles. Since the catalyst particles are confined to the combustion surface, it is possible to assume that the gap between APC and catalyst particles is approximately equal to the radius of the latter on the combustion surface and as it advances toward the combustion surface it smoothly decreases to zero at a distance less than or equal to the diameter of the catalyst particle (figure 3c shows the form of the funnel constructed on the basis of the facts mentioned above).
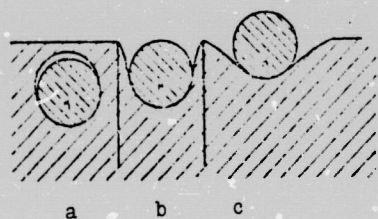

Figure 3. Various phases of the development of a cavity around CuO catalyst particles moving toward the combustion surface.

From here it follows that the thickness of the sub-surface layer where the catalyst works most effectively is less than or equal to 10-20 μm, in the given case. Apparently, as a catalyst particle moves toward the combustion surface a cavity is formed around it inside which products of APC decomposition are accumulated, which leads to a significant increase of pressure inside the cavity. This cavity is revealed when the thickness of the APC wall between the cavity and the combustion surface becomes less than critical (during which destruction of the wall occurs). Various phases of this process are shown in figures 3a, b, c. Similar traits (formation of funnels around catalyst particles, etc.) were also observed during the combustion of a stoichiometric mixture of APC (2 μm) with PMMA in the presence of 2% copper chromite.

The effect of catalyst dispersion on the effectiveness of its action during the combustion of a model mixture composition with APC and PMMA as a base. The combustion rate of compositions (the preparation procedure of specimens is similar to [1, 5, 6]) was determined in a bomb of constant volume in an atmosphere of nitrogen with registration of the combustion time by recording the curve of the pressure change caused by the combustion of a specimen. Catalysts of various dispersions were obtained by annealing, in air, ferric oxides at various temperatures from 350 to 1000°C.

During the annealing of a catalyst, caking of its particles occurs. The dispersion of the catalyst was determined, on the one hand, from data on the specific surfaces of the catalysts and, on the other hand, by the electron-microscope investigations of the average dimensions of catalyst particles in the powder and in the fuel. These data are the same for particles with $r_k > 0.1$ μm. Only in the case of highly-dispersed specimens of catalysts with specific surface ~100-30 m^2/g was there adhesion of primary particles measuring ~0.01 μm with the formation of larger agglomerates of these particles ~0.1 μm (and in several cases still coarser). In the case of certain Fe_2O_3 specimens with r_k~0.1-0.2 μm an even distribution of k-phase catalyst particles was recorded.

Figure 4 presents the results of measurement of the dependence of the effectiveness of catalyst action $z-1=\dfrac{u_k-u_0}{u_0}$ (where u_k and u_0 are the combustion rates of compositions with and without a catalyst) on the average catalyst radius r_k, calculated by the formula

$$r_\kappa = \frac{3}{S_{уд}},$$

where $S_{уд}$ is the specific catalyst surface determined by the method of argon heat desorption. As is seen from the figure, the form of
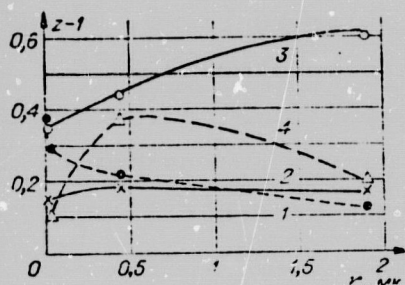
Figure 4. Dependence of the effectiveness of catalyst action z-1 on its dispersion during the combustion of APC and of a stoichiometric mixture composition.
1 - APC (2 μm)+PMMA (3 μm)+1% Fe_2O_3 at 60 atm (u_0=14.3 mm/sec; 2 - APC (200 μm)+PMMA (3 μm)+1% Fe_2O_3 at 60 atm (u_0=6.5 mm/sec; 3 - APC (2 μm)+1% Fe_2O_3 at 80 atm (u_0=7.9 mm/sec; 4 - APC (200 μm)+1% Fe_2O_3 at 80 atm (u_0=8 mm/sec).

the curves z-1 vs r_k is different for APC and for a mixture composition, and also depends on the dispersion of APC. The dependence of z-1 on r_k is different from that predicted by the theory of an extremely strong catalyst in the gas phase ($z-1 \sim r_k^{-1}$). It agrees more with that dependence which follows from the model developed in [10], where catalyst action is taken into account in both the gas and the condensed phase. This model, originally developed for catalysis of monopropellant combustion (relative to APC) can be applied also to the combustion of "homogeneous" APC-based mixtures (when the dimensions of the oxidizer and fuel particles are small enough that diffusion mixing of the primary products of pyrolysis of the oxidizer and binder are not the limiting stage). The calculation in [10] shows that during the work of the catalyst in the diffusion region, the effectiveness of its action in the k-phase exceeds by more than one order the effectiveness of the action in the gas phase. This also results from the following elementary estimates. The ratio of times τ_k and τ_{ra3} that the catalyst particles remain in the effectively working near-surface layer of the k-phase (width L_k) and in the preheating zone in the gas phase (width L_r) equals

$$\frac{\tau_k}{\tau_{ra3}} = \frac{\rho_k}{\rho_{ra3}} \frac{L_k}{L_{ra3}},$$

where ρ_k and ρ_{ra3} are condensed- and gas-phase densities. If we assume L_k=5-10 μm and L_{ra3}=10-50 μm, at 40 atm pressure τ_k/τ_{ra3}=100-40. Since the distance between catalyst particles in the k-phase is ρ_k/ρ_{ra3} times less than that between catalyst particles in the gas phase, in the diffusion region the ratio of gas diffusion time to a catalyst particle linked with the k-phase and to a catalyst particle in the gas phase will be no more than ρ_{ra3}/ρ_k. However, the ratio of residence time to diffusion time is what determines the effectiveness of catalyst action in the diffusion regime. As can be seen, this ratio is significantly higher for catalyst particles linked with the k-phase than for particles in the gas phase.

The microscope and electron-microscope investigations conducted above confirm the point of view which states that the catalyst works highly effectively in the k-phase (the presence of funnels around catalyst particles in the case of cupric oxide). The formation of a catalyst particle frame (in the case of Fe_2O_3) protruding 10-20 μm over the combustion surface should also lead to an increase in the effectiveness of its action near the k-phase surface (because of the rise of effective catalyst concentration in this gas phase region compared with that which occurs 10-20 μm from the k-phase surface). If the distance from the k-phase surface to the flame zone is 50-100 μm, it can be considered that the catalyst works effectively close to the k-phase, which can be recorded by measurements of the effective heat release zones using thin thermocouples. However, the flame zone is 10-20 μm from the fuel surface, the k-phase (which includes the catalyst particle frame) is in the flame zone. Consideration of this circumstance should reconcile researchers having opposing points of view in their dispute about the place of catalyst action during the combustion of condensed systems.

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